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On Board Corrosion Analysis of a Recovered Nuclear Waste Container

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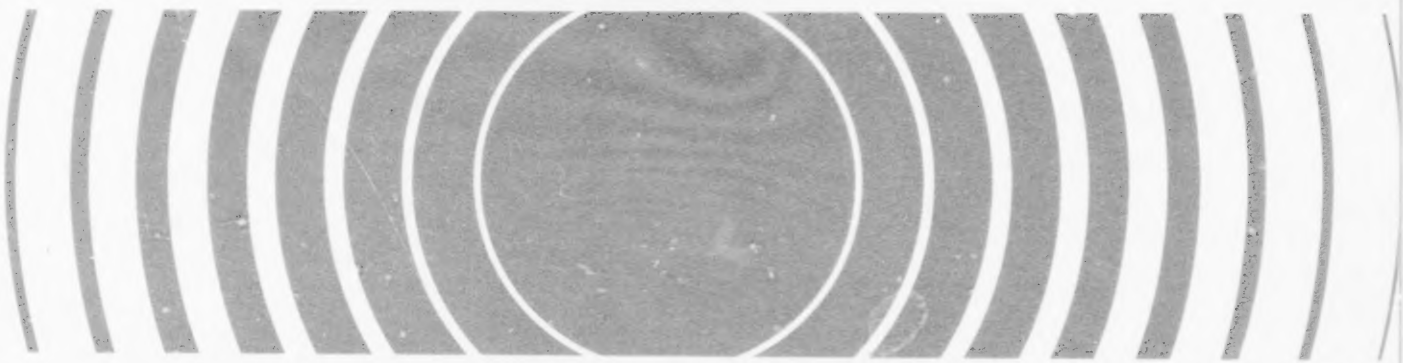

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16. Abstracts
This report represents intial observations on extent of corrosion of an 80-gallon low-level radiactive waste container after immersion for more than fourteen years. This container was recovered during the 1976 survey of a deepsea radioactivewaste dumpsite located at a depth of 2800m in the Atlantic. During the two hour interval between the time the container first emerged from the ocean until it was encapsulated, the exterior condition of the metal drum, including the appearance of corrosion product films and attached biological organisms, was photographically documented. Representative photographs as well as results of limited chemical and biological analyses are presented. These results are then discussed with respect to previously published deep ocean corrosion data, and recommendations are given for improving shipboard sampling and analytical procedures.

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TECHNICAL NOTE
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ON BOARD CORROSION ANALYSIS OF A RECOVERED NUCLEAR WASTE CONTAINER

by

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August 1979

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The following reports are part of the EPA/ORP 1976 Ocean Disposal Report Series:

ORP/TAD-79-1 Materials for Containment of Low-Level Nuclear Waste in the Deep Ocean

ORP/TAD-79-2 On Board Corrosion Analysis of a Recovered Drum from the Atlantic 2800 Meter Radioactive Waste Disposal Site

ORP/TAD-79-3 Analysis and Evaluation of a Radioactive Waste Package Retrieved from the Atlantic 2800 Meter Disposal Site

ORP/TAD-79-4 Reports of Infaunal Analyses Conducted on Biota Collected at the Atlantic 2800 Meter Radioactive Waste Disposal Site

ORP/TAD-79-5 Geologic Observations of the Atlantic 2800 Meter Radioactive Waste Dumpsite

ORP/TAD-79-6 Sediment Geochemistry of the 2800 Meter Atlantic Radioactive Waste Disposal Site

ORP/TAD-79-7 Ocean Current Measurements at the Atlantic 2800 Meter Radioactive Waste Disposal Site

ORP/TAD-79-8 Survey Coordination and Operations Report - EPA Atlantic 2800 Meter Radioactive Waste Disposal Site Survey

ORP/TAD-79-9 1976 Site Specific Survey of the Atlantic 2800 Meter Deepwater Radioactive Waste Dumpsite: Radiochemistry

ORP/TAD-79-10 Sediment Characteristics of the 2800 Meter Atlantic Nuclear Waste Disposal Site

FOREWORD

The Environmental Protection Agency, (EPA), was given a Congressional mandate to develop criteria, standards, and regulations governing the ocean disposal of all forms of wastes pursuant to Public Law 92-532, the Marine Protection, Research and Sanctuaries Act of 1972. Within this Congressional mandate, EPA has initiated a specific program to develop regulations and criteria to control the ocean disposal of radioactive wastes.

EPA has taken an active role both domestically and within the international nuclear regulatory arena to develop the effective controls necessary to protect the health and safety of man and the marine environment. The EPA Office of Radiation Programs (ORP) initiated feasibility studies to determine whether current technologies could be applied toward determining the fate of radioactive wastes dumped in the past. After successfully locating actual radioactive waste containers in three of the primary radioactive waste disposal sites used by the United States in the past, ORP developed an intensive program of dumpsite characterization studies to investigate the following: (a) the biological, chemical and physical parameters, (b) the presence and distribution of radionuclides within these sites, and (c) the performance of past packaging techniques and materials.

These studies have provided needed information and data on the past and present nuclear waste disposal activities concomitant with the growing national and international concern for the long-term effects of this low-level waste disposal option.

ORP has now completed the fifth in a series of Pacific and Atlantic Ocean dumpsite surveys which began in 1974. This survey of the Atlantic 2800 meter deep-sea radioactive waste disposal site, which is centered at coordinates 38°30'N, 72°06'W and located approximately 120 miles east of the Maryland-Delaware coast, was conducted in June 1976.

A major objective of this 1976 Atlantic survey was the first recovery of a steel and concrete container from any deep-sea dumpsite. In conjunction with the survey, EPA/ORP initiated a contract study to evaluate, prior to extensive laboratory analysis, the chemical, biological and corrosion status of the exterior of the container immediately upon recovery. The following report presents this evaluation.

Readers of this report are encouraged to inform the Director, Technology Assessment Division (ANR-459), Office of Radiation Programs, U.S. Environmental Protection Agency, Washington, D.C. 20460, of any errors, omissions, or other comments.

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Abstract

During the 1976 Atlantic 2800m radioactive waste dumpsite survey, an 80-gallon low-level radioactive waste container was recovered. Within the two hour interval between the time the container first emerged from the ocean until it was encapsulated, the exterior condition of the drum, including the appearance of corrosion product films and attached biological growths, was extensively documented photographically. In this report, representative photographs, as well as the results of limited chemical and biological analyses performed by University of Delaware personnel during the above two hour interval, are presented. These results are discussed in light of previously published deep ocean corrosion data, and recommendations on improving shipboard sampling and analytical procedures are given.

1.0 INTRODUCTION

On July 31, 1976, an 80-gallon nuclear waste container was recovered by the Environmental Protection Agency from a depth of 2783 meters in the Northwestern Atlantic Ocean at a point approximately 120 miles east of the Delaware-Maryland border. The container was hoisted aboard the research vessel, Cape Henlopen, where it was photographed, and samples were immediately taken of corrosion products and attached biological growths. The container was then encapsulated in a jet engine shipping container which was flushed thoroughly with argon to minimize any further corrosion. The elapsed time from when the container first broke the surface of the water to the start of the argon flushing process was two hours.

The purpose of this report is to describe the photographic, chemical, and biological analyses performed on board the ship by University of Delaware personnel during those two hours and to present the results of those analyses.

2.0 EXPERIMENTAL METHODS

Both the surface condition of the container as it came on board the ship, and the recovery operation itself, were documented photographically. Thirty-five mm color slides of the container were taken as soon as it broke the surface in order to record the volume and distribution of corrosion products before any changes due to decreasing pressure and increasing temperature took place. After the container was secured to the deck of the ship, photographs were taken in a systematic way so that they could be related to the correct position on the exterior of the drum upon subsequent laboratory examination.

Close-up photographs were taken of all interesting features including biological growths. Close-up photographs were located with respect to the container by taking photo pairs. First, an overall picture was taken of the container with a cut-out cardboard frame held over the feature of interest. The camera was then repositioned and a close-up photograph was taken of the area within the frame. The photographs presented in this report were printed from color plates made from selected original color slides.

The pH of the corrosion products and the mud layer, where it was still clinging to the drum, was spot checked at several locations while the drum surface was still wet. Readings were taken with pH indicator papers and recorded for each location.

Samples of the corrosion product were taken both from the outer layers (reddish orange) and from the layer immediately adjacent to the bare metal surface (greenish black) at a location just above the mudline on the cylindrical surface near the metal end and were examined for bacterial activity. The examination was done both immediately on board the ship as well as subsequently ashore in the laboratory. A Unitron BPH phase contrast microscope was used for all observations. The samples observed on board were examined directly at 600X by spreading the moist sample on a glass slide. These observations were very difficult due to ship roll and vibration. The samples to be observed in the laboratory were diluted with seawater that had been passed through a 0.22 um membrane filter (Millipore) and encapsulated in glass vials to prevent them from drying. In the laboratory, these samples were spread between a glass slide and coverslip and examined in phase contrast

at 1500X using an oil immersion lens. No special measures were taken to avoid bacterial contamination of the sample nor were aseptic techniques used in preparing the filtered seawater.

3.0 RESULTS

3.1 Photographic Analysis

Figure 1 is a schematic diagram of the container showing the locations from which each of the photographs in Figures 2 through 9 were taken. Figures 2 through 9 show the general condition of the container immediately upon recovery. Note that the container as it sat on the deck was upside down compared to its position on the sea floor.

Figure 2a shows the concrete end of the drum seconds after it first broke the surface of the water. The identifying markings on the concrete end are legible in Figure 2b and include such information as the package number (28), the volume of the waste-matrix mixture (9.0 cubic feet), the weight of the package (1682 pounds), the most hazardous isotope present in the package (cobalt-60) and the dose rate at the surface of the drum at the time of packaging (3 millirads/hour). Information not clearly visible in Figure 2(b) indicated that the radioactive waste package was prepared in 1961. Prior to the start of recovery operations the drum sat partially embedded in the bottom sediments. The sediment line is clearly visible in Figure 2, the black portion of the concrete end having been in the mud.

Figures 3a and 3b show the surface condition of the container after hoisting out of the water but before securing on deck. There was a 10 to 15 minute interlude here while the radioactivity level of the drum was being measured. As seen in the photographs, the container is in remarkably good condition after 14-15 years of immersion. The mud line can again be seen in Figure 3b between the two arrows. Note that the upper half of the drum, which was below the mud line, is less corroded than the lower half which was exposed to the water column. The view in Figure 3a, for instance, shows most of the area that was in the mud, and there is very little corrosion visible. Identical areas on the drum surface are labeled "A" and "B" on Figures 3a and 3b. On seventy-five percent of the metallic surface area of the drum (and on considerably more of the area below the mud line) the original black enamel finish was still intact.

Several of the more interesting areas of the container surface were photographed in detail after the container was secured on deck. These are shown in Figures 4 through 9. Figure 4 shows the surface above and below the mud line on the left portion of the cylindrical surface of the drum as seen in Figure 3b. The large area of bare metal surface showing there as well as the bare metal showing on the raised ribs of the drum in Figures 3a and 3b were probably scraped clean as the drum was dragged along the bottom during the initial part of the hoist precedure. There is little doubt that this happened, as the track of the drum where it was dragged along was clearly visible from the deep submersible, Alvin, upon subsequent inspection of the site.

Figure 5 shows the heavy concentration of corrosion products just to the lower right of the letter "A" in Figure 3b. By the time this picture was taken, some of the corrosion product had been scraped off into sample bottles. Other portions of it had rubbed off against the nylon webbing, visible in Figure 5, which had been installed as an additional aid to handling shortly after the picture in Figure 3b was taken. There was no attempt made at this time to scrape all the way through the corrosion product layer to determine the condition of the underlying metal as this was planned for subsequent laboratory operations.

The outer steel container was in the worst condition around the rim at the concrete end as shown in Figure 6. There was no marked difference in the condition of the rim above as opposed to below the mud line. A sample of the corroded edge of the metal was clipped off with metal shears for later examination at the Brookhaven National Laboratory.

When the container first arrived at the surface, it was apparent that there was a perforation in the metal drum as a stream of seawater was observed coming out as if under pressure. The stream can be seen just below the letter "B" in both Figures 3a and 3b. The area from which the stream came was below the mud line and is shown close up in Figure 7. By the time this photograph was taken, the pressure had nearly equalized and the remaining liquid was seeping out as shown. Some of this liquid was collected by the EPA Project Officer for subsequent laboratory analysis. Upon further examination with a probe, it became apparent that the perforation was not due to corrosion but was a recent puncture. It is suspected that this occurred as the drum was being dragged along the bottom as related above.

Figures 8a and 8b show the condition of the metallic end of the drum. The mud line runs between the two arrows from upper right to lower left of Figure 8a, the portion to the upper left having been buried in the bottom sediments. The corroded area in the center of the metallic end is shown in Figure 8b. This appearance is typical of a painted steel surface in the early stages of seawater corrosion. The small white streaks near the lower rim of the metallic end as seen in Figure 8a were the only macroscopic biological growths that were found attached to the drum. They were sampled and identified as polychaete tubes under separate contract by Dr. Donald Reish of California State University.

There was very little corrosion below the mud line. Where corrosion did take place, it appeared to be highly localized as in Figure 9. Instead of being spread uniformly over the surface, the corrosion took place in the form of broad shallow pitting (see arrows). It is estimated that the depth of attack was 0.2 to 0.5 mm. As there were no corrosion products associated with these pits upon recovery of the drum, one can only assume that the products were scraped off as the drum dragged along the bottom. This is a reasonable assumption as this portion of the drum was below the mud line prior to recovery.

3.2 Chemical Analysis

The pH of the corrosion products was measured with pH indicating paper at several locations both above and below the mud line. The pH was generally

found to be between 6 and 8. There was one notable exception. The pH of the water bubbling from the puncture described in connection with Figures 3 and 7 was between 13.0 and 13.5.

3.3 Microbiological Analysis

Despite the fact that aseptic techniques were not used in sampling the corrosion products, no microorganisms could be positively identified microscopically as being present in the corrosion products. Both the red-orange outer layer and the greenish-black inner layer adjacent to the bare metal surface were examined. Since the shipboard observations were very difficult due to vibration problems, observations were also made in the laboratory. The same negative result was obtained.

4.0 DISCUSSION

The overall condition of the container that was recovered was much better than might have been expected given the duration of exposure in the deep ocean (probably in excess of 14 years). The often localized nature of the corrosion that did take place was also somewhat surprising as one normally expects steel structures to be corroded uniformly over the exposed surface. Before drawing any conclusions about the significance of the good condition of the drum to future ocean dumping, however, two things must be considered: first, this is only a single data point; second, this single point is purposely biased. Many of the containers observed by the submersible, Alvin, were in worse condition than the one recovered. This particular drum was selected for recovery because it appeared to be in good enough condition to survive the trip to the surface and yet provide meaningful information on past packaging performance.

The corrosion rate of uncoated plain carbon steel in aerated quiescent seawater is normally as high as 0.25 to 0.40 mm/year (10 to 16 thousandths of an inch per year [MPY]) for the first few months of immersion[1,2,3]. Gradually, as the fouling and corrosion product layer builds up, the above rate decreases[2] to 0.03 to 0.13 mm/year (1 to 5 MPY). In addition, this rate depends directly on the concentration of dissolved oxygen present in the seawater[4] and on the pH of the seawater[4]. Within the range of pH 4 to 10 the corrosion rate of steel is independent of pH and depends only on how rapidly oxygen can be supplied to the steel surface. As the pH becomes more basic than 10, however, steel becomes passive in seawater and the corrosion rate drops rapidly to a negligible value[4].

The well known corrosion behavior of steel in seawater described above may partially account for the good condition of the recovered nuclear waste container. Although dissolved oxygen measurements were not made at the drum recovery site, it is generally found that the dissolved oxygen in the deep ocean decreases rapidly with depth from 7 ppm at the surface to a minimum of about 0.5 ppm at 750 meters, then rising again typically to 2 or 3 ppm at great depth. Occasionally the dissolved oxygen at great depth may rise again to a value as high as that at the surface or even higher.

Given the good condition of the recovered drum, it can be speculated that the dissolved oxygen in both the water and the sediments at the drum recovery site was low (perhaps 1 to 2 ppm). This, coupled with the low temperature to be expected at great depth, would account for the relatively low corrosion rates observed. In addition, the concrete inside the drum was saturated with

seawater, and its pH was reported in the results section to be between 13 and 13.5. This is consistent with other measurements reported for the pH of seawater in concrete[5]. The corrosion rate of the steel on the inner surface of the container should, therefore, have been negligible and corrosion should have proceeded from the outside only. The difference that this can make is illustrated by the fact that the steel container was in the worst condition around the rim at the concrete end where the steel extending beyond the concrete by about two centimeters was exposed to ambient pH seawater on both sides. The perforated condition of the steel in that area was shown in Figure 6.

The corrosion rate of steel in seawater is not usually influenced significantly by the presence (or absence) of microorganisms. The one noticeable exception to this is in anaerobic bottom sediments where the corrosion rate of steel normally is negligible. If sulfate reducing bacteria are present, however, they allow the formation of a loosely adherent FeS scale on the steel which is cathodic to the bare metal surface[4,6]. This produces a galvanic couple which accelerates the corrosion of the steel and is accompanied by hydrogen evolution. The excellent condition of the portions of the recovered drum that were buried in the sediments testifies that sulfate reducing bacteria were probably not active in sediments in the recovery area. This view is also supported by the negative result of the microscopic investigations reported in the results section. If sulfate reducing bacteria had been active, we should have been able to detect them in the corrosion products.

5.0 RECOMMENDATIONS AND CONCLUSIONS

It is not possible based on the one container that was recovered to make any definitive conclusions about the suitability, from a corrosion viewpoint, of this method of packaging nuclear wastes for ocean disposal. It is possible to say that at least one of the many containers dumped 16 to 20 years ago survived its stay on the bottom with the exterior in reasonably good condition.

It is also possible to make recommendations for increasing the value of future work of this type:

1. Determine the dissolved oxygen concentration both in the water column within about ten meters of the bottom and in the upper one meter of the sediments at the dumpsite. This should be done both several months before and again several months after, as well as at the time of the survey (total of three measurements with at least six months from the first to the last), in order to detect if there is any variability. This type of data, which was not available for the work reported here, would have allowed a more meaningful corrosion analysis. The expected corrosion rate could have been estimated more accurately and related directly to other published deep-sea corrosion data.

2. Retain the services of a qualified marine microbiologist to test the sediment samples for the presence of microorganisms. The sulfate reducing bacteria are particularly important for evaluating the corrosion behavior. Also have this person arrange to test the corrosion products for bacterial activity by culturing techniques as well as by microscopy.

The above recommendations should be extended to include not only research on the effects of past dumping, but also research on sites that may be under consideration for future dumping. In this way it will be possible to detect and eliminate sites whose characteristics might accelerate deterioration of the container by corrosion.

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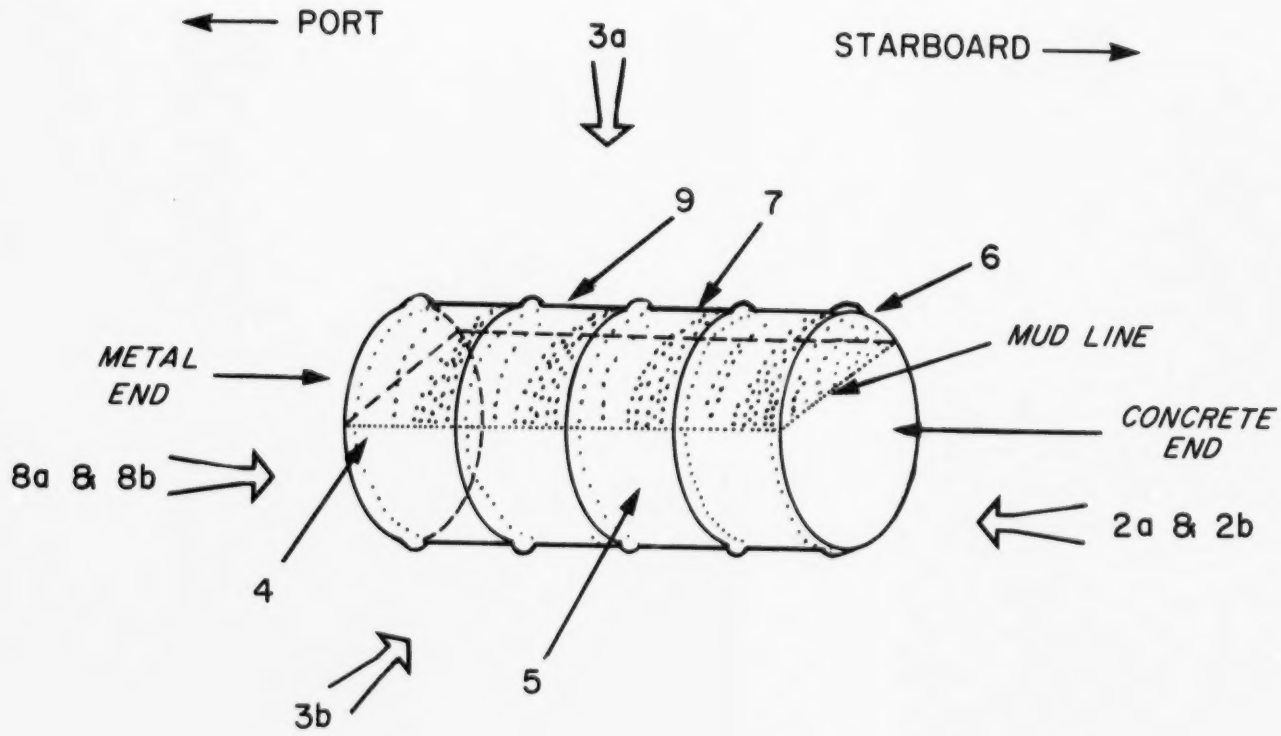
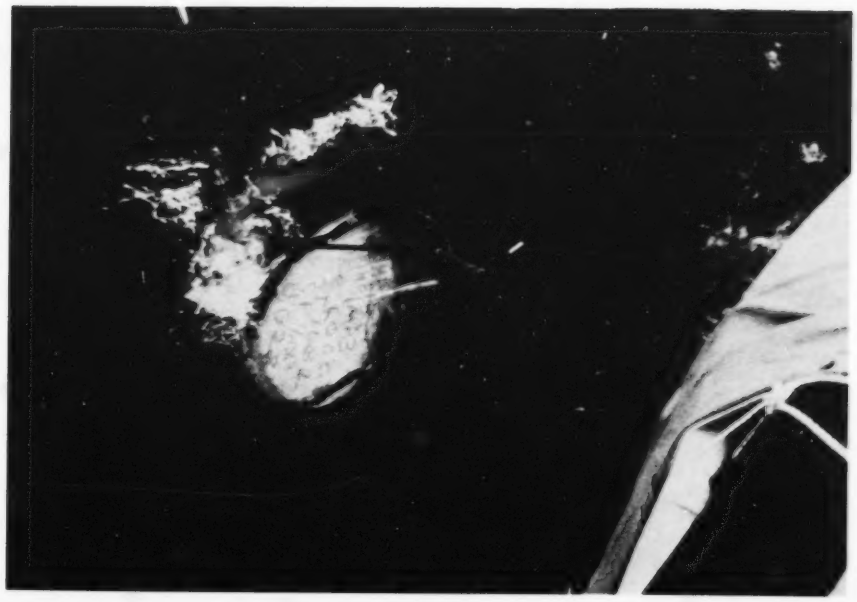


Figure 1. Schematic diagram of the recovered container showing the locations of the photographs in Figures 2 through 9. The container as it sat on the deck, and as pictured here is upside down compared to its position on the sea floor. The shaded portion was embedded in the sediments.

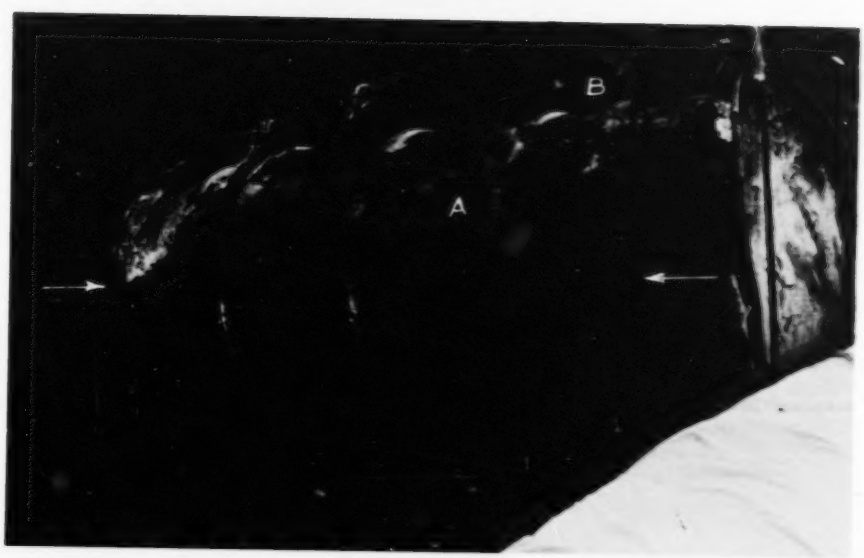


(a)

(b)

Figure 2. Nuclear waste container. a) a few seconds after breaking surface of water, b) identification marks on concrete end.

(a)



(b)

Figure 3. Nuclear waste container showing: a) portion of surface that had been buried in the sediments, and b) the mud line between arrows.

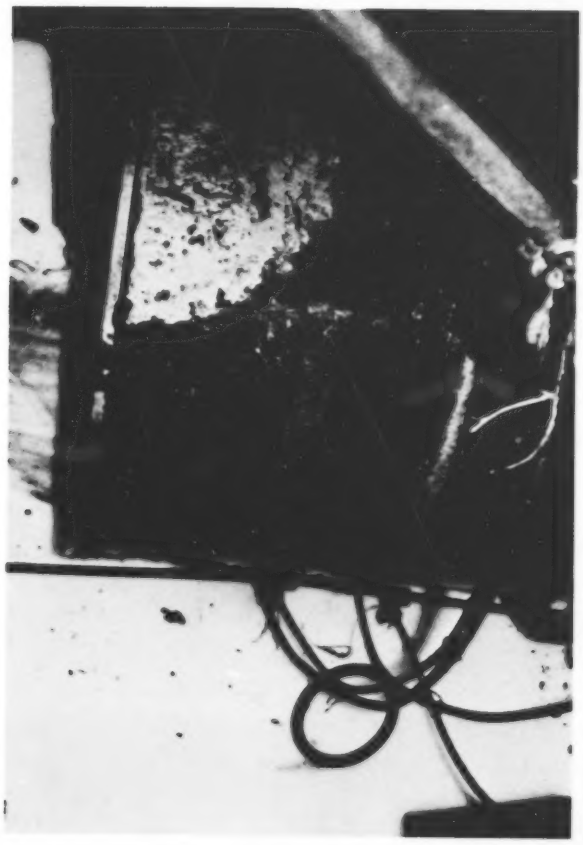


Figure 4. Left end of cylindrical surface of nuclear waste container as seen in Figure 3(b) after securing on deck.

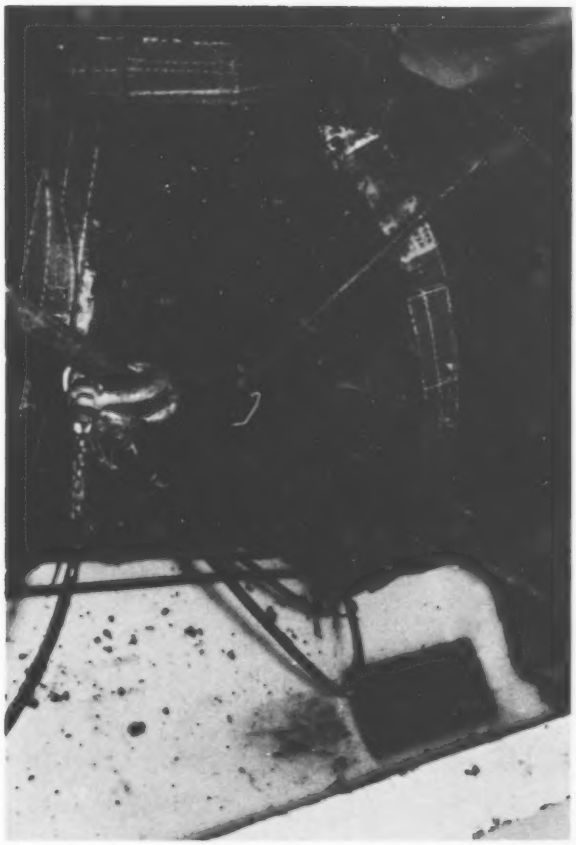
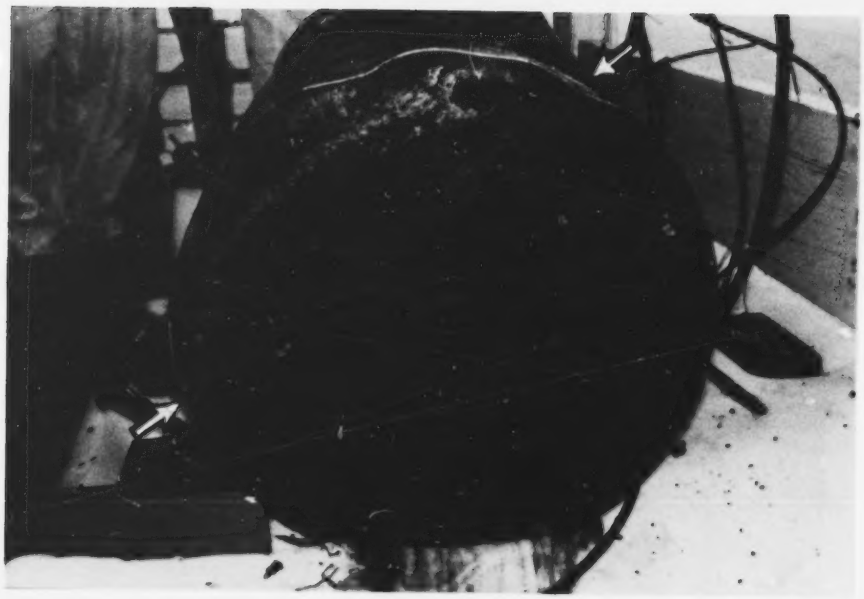


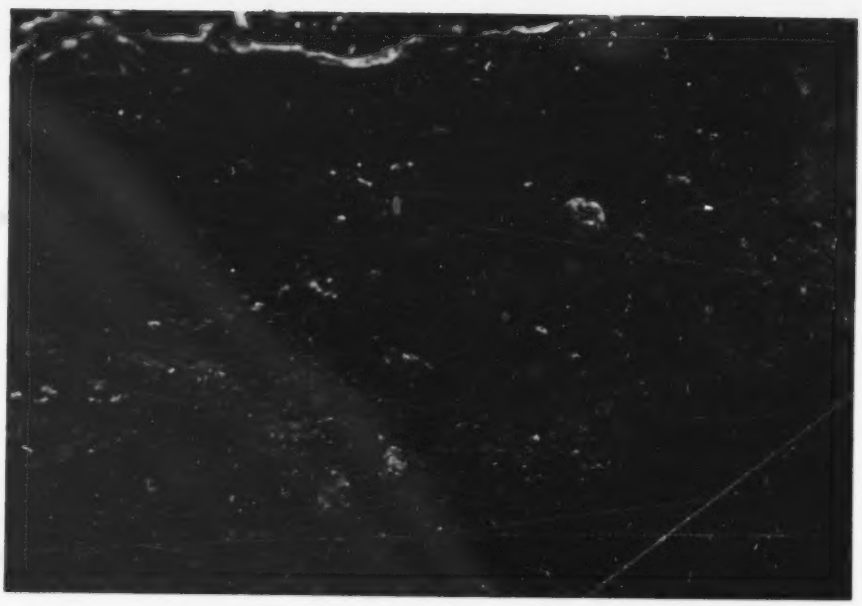
Figure 5. Heavily corroded portion of cylindrical surface of container just to the lower right of letter "A" in Figure 3(b).

Figure 6. Corrosion around the rim of the concrete end of the container.

Figure 7. Water oozing out of perforation on cylindrical surface of container. Location of the perforation is just below the letter "B" in Figure 3(a) and (b).



(a)



(b)

Figure 8. Metallic end of nuclear waste container: a) mud line is shown between arrows, b) close up of corroded portion.

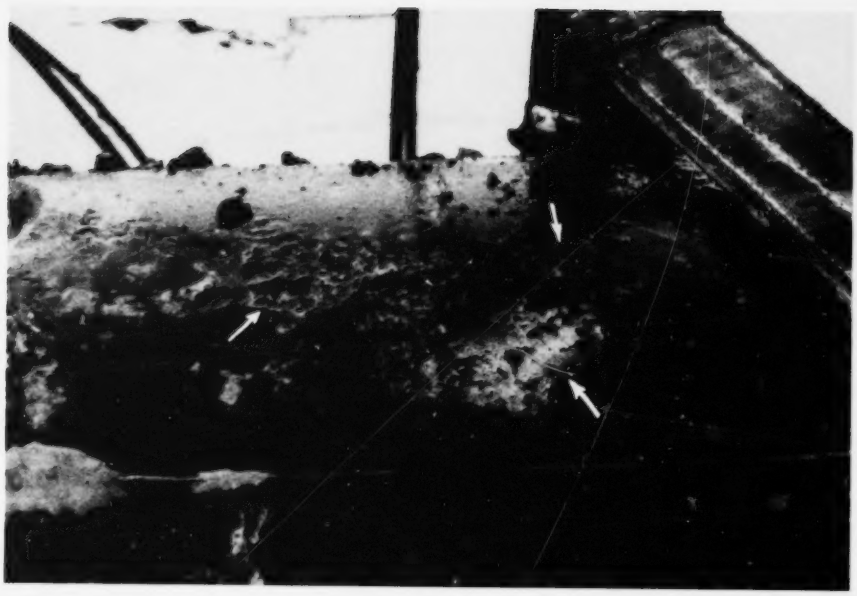


Figure 9. Localized corrosive attack (see arrows) on cylindrical surface below the sediment line.